PERMSELECTIVE MEMBRANES FOR THE
REMOVAL OF H$_2$S FROM COAL GAS

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## INTRODUCTION

The integrated combined cycle power plant firing low BTU coal gas is one of the most attractive and efficient systems for production of electricity from coal.  H$_2$S must be removed from the fuel gas stream when high sulfur coal is used in order to meet emissions requirements.

A permselective membrane which can be used to selectively separate H$_2$S from low BTU coal gas is being developed.  The membrane is based on the principle of facilitated transport in which permeation is augmented by reversible chemical reaction with a carrier species incorporated in the membrane.  In the case of facilitated H$_2$S transport, the liquid membrane is a film of immobilized carbonate solution with which H$_2$S reacts, yielding permeation rates and selectivities orders of magnitude greater than those of conventional polymeric membranes.

## MEMBRANES FOR GAS SEPARATIONS

Membrane gas separations are attractive because they are fundamentally simple and can require less energy than conventional techniques.  However, due to their generally low permeation rates and selectivities, the application of membranes to industrial gas separations has been limited.  Low permeabilities result in excessively large membrane area requirements reflected in high capital costs. In order to achieve an adequate degree of separation with a membrane of low permselectivity, resort to multiple stage membrane cascades may be required, and both high capital and operating costs accompany this type of operation.  To overcome these objections, General Electric is developing a new class of membranes called facilitated transport membranes, which promise both high permeation rates and high selectivity.

Permeation of gases through non-porous polymeric films occurs by a solution/diffusion mechanism.  The permeant molecule first dissolves in the membrane phase and then diffuses across the film driven by its concentration gradient.  The permeability of such a membrane is given by the product of permeant solubility and diffusivity

$$Pr = D_i \cdot S_i \tag{1}$$

where permeability is generally defined by the equation

$$Pr_i = \frac{N_i \cdot \delta}{A \cdot \Delta P_i} \quad [=] \quad \frac{(cc/sec) - cm\ thickness}{cm^2 - cm\ Hg\ \Delta P} \tag{2}$$

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■ and

$D_i$ = diffusivity of permeant i in the membrane, $cm^2$/sec

$S_i$ = permeant solubility, cc(STP)/cc membrane-cmHg

$N_i$ = permeant flux, cc(STP)/sec

$A$ = membrane area, $cm^2$

$\delta$ = membrane thickness, cm

$\Delta P_i$ = transmembrane partial pressure difference, cm Hg

Membrane selectivity is expressed in terms of a separation factor which is simply the ratio of the permeation coefficients of two gases

$$\alpha_{ij} = Pr_i/Pr_j \qquad\qquad 3)$$

Unfortunately, both solubilities and diffusivities of gases in polymeric films are generally low and thus gas permeabilities are likewise low. Furthermore, since gas diffusivities and solubilities do not vary greatly for a given polymer, conventional polymeric solution/diffusion membranes also exhibit limited permselectivity as a rule.

Reasonable fluxes and area requirements can be obtained with relatively low performance membrane materials by employing ultrathin membrane technology, and silicone rubber and its copolymers have a number of useful applications when used in this form (1,2,3). Nonetheless, the problem of low selectivity is not resolved by decreasing membrane thickness.

A considerable improvement in performance results from using an immobilized liquid as the membrane phase rather than a polymer. Transport through the "immobilized liquid membrane" (ILM) again occurs by the solution/diffusion mechanism, but permeation rates are now improved because solubilities and diffusivities of permeating gases are generally higher in the liquid phase than in polymers. By immobilizing the membrane liquid by impregnation of a suitable porous support material, it is possible to combine the desirable permeation properties of the liquid with the physical properties and ease of handling of the polymeric support membrane. Such a membrane consisting of a supported polyethylene glycol film has been shown to have high permeability and selectivity for sulfur dioxide (4).

## FACILITATED TRANSPORT

A more significant feature of immobilized liquid membranes may be that permeabilities and selectivities for gases in liquid membranes can further be augmented, often by orders of magnitude, through facilitated transport. This involves a non-volatile carrier species in the liquid membrane which reacts reversibly with the permeating gas. The reactive carrier shuttles back and forth between opposite sides of the membrane carrying the permeant with it in one direction. This process is very common in biological systems (5).

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Consider the simplest case of facilitated transport in which a single permeating species, A, reacts reversibly with a carrier, C, to form a complex, AC; neither the carrier nor the carrier-permeant complex can cross the membrane boundaries.  The sequence of events describing facilitated transport is the following:

(1)  Species A dissolves in the membrane liquid;

(2)  A reacts with the carrier near the feed side membrane boundary;

(3)  The AC complex (as well as "free" A) diffuses across the immobilized liquid film;

(4)  Near the other membrane boundary where the partial pressure of A is low, the reaction equilibrium shifts and the AC complex dissociates;

(5)  Free A comes out of solution;

(6)  The carrier diffuses back across the membrane and is again available to participate in the facilitated transport cycle.

The total flux of A is the sum  of that by simple diffusion (as free A) and by facilitated diffusion (as AC).  Because the concentration levels and gradients in carrier and complex can be made orders of magnitude greater than those of the "free" permeating component, transport of A can be dramatically enhanced by the carrier process. Moreover, membrane selectivity can be extraordinary, as advantage can be taken of the specificity of chemical reaction.

Some of the earliest work by engineers to exploit the separative efficiency of facilitated transport membranes is that of Ward and Robb (6), who identified the use of an aqueous carbonate solution immobilized in a cellulose matrix as a $CO_2$ transport membrane.  They found that not only was $CO_2$ transport enhanced by orders of magnitude as compared to diffusion through water films, but also that the transport rate could further be enhanced by the addition of a hydrolysis catalyst.  A number of mathematical analyses of facilitated transport have been published, including those by Ward (7) and Shultz et al (8).

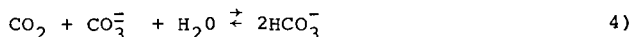### FACILITATED TRANSPORT OF $H_2S$

Facilitated transport of $H_2S$ occurs in liquid membranes consisting of aqueous carbonate solutions according to the following process (refer to Figure 1):

(1)  $H_2S$ dissolves in the membrane liquid at the high-pressure (h.p.) side of the film;

(2)  $H_2S$ decomposes near the h.p. side of the film by the reaction $H_2S \rightarrow H^+ + HS^-$;

(3)  $H^+$ produced in step (2) is consumed by $CO_3^=$ that is diffusing toward the h.p. side by the reaction $H^+ + CO_3^= \rightarrow HCO_3^-$;

(4)  $HS^-$ and $HCO_3^-$ diffuse from the h.p. to the low pressure (l.p.) side of the film;

(5) $HS^-$ combines with $H^+$ near the l.p. side of the film by the reaction $HS^- + H^+ \rightarrow H_2S$;

(6) $H^+$ for step (5) is supplied by $HCO_3^-$ by the reaction $HCO_3^- \rightarrow H^+ + CO_3^=$;

(7) $CO_3^=$ produced in step (6) diffuses back to the h.p. side;

(8) $H_2S$ produced in step (5) leaves the membrane.

Carbon dioxide also reacts with the membrane liquid as described by the overall reaction

$$CO_2 + CO_3^= + H_2O \overset{\rightarrow}{\underset{\leftarrow}{}} 2HCO_3^- \qquad\qquad 4)$$

and, accordingly, it also experiences facilitated transport. However, because the reaction rate of $CO_2$ with the membrane liquid is slow relative to that of $H_2S$, alkaline absorbents demonstrate an inherent selectivity for absorption of $H_2S$ in preference to $CO_2$. A means of improving this $H_2S/CO_2$ selectivity still further will be described later.

In its present configuration, the immobilized liquid membrane for facilitated $H_2S$ transport consists of a concentrated (25-30 wt. %) aqueous solution of $K_2CO_3$, although other membrane liquids including $K_3PO_4$ solutions have been screened. The membrane liquid is immobilized as a film a few thousandths of an inch thick by virtue of surface tension forces in the pores of a hydrophilic polymeric support membrane.

Two approaches have been pursued for maintaining the transmembrane $H_2S$ partial pressure gradient which drives membrane transport. The first and simplest involves "sweeping" one face of the membrane with low pressure steam to dilute the acid gases which permeate across the membrane and keep their partial pressures low. The sweep steam carries the acid gases from the membrane permeator to a condenser, providing a dry mixture of $H_2S$ and $CO_2$ at a pressure sufficient for conversion of $H_2S$ to elemental sulfur in a Claus plant or similar process. It is convenient to visualize the liquid membrane functioning as both the $H_2S$ absorption column and steam stripping column which are conventionally used for $H_2S$ removal. $H_2S$ absorption and solution regeneration occur within the membrane liquid film thickness rather than in two separate vessels operated at different pressures with absorbent pumped between them. A drawback to steam sweeping is that a high pressure difference corresponding to the difference between the gasification pressure and the sweep steam pressure must be supported across the liquid film. While the membrane support problem is significant, it is indeed feasible to operate liquid membranes under such conditions, and the steam sweeping approach is being pursued in a parallel program. However, an alternative affords greater $H_2S$ membrane reliability.

The alternative involves sweeping permeated acid gases from the membrane permeator by means of a pressurized liquid which is an $H_2S$ absorbent. This liquid sweep may simply be a concentrated solution of $K_2CO_3$, identical in composition to the immobilized membrane liquid, which is isolated from the liquid membrane sandwich by a layer of non-wetted microporous polymer membrane which affords no significant resistance to $H_2S$ transport. Relatively little power is required to pressurize the sweep

liquid to coal gas pressure, and by this means no significant pressure difference is applied across the membrane. The price of avoiding the membrane support problem is, of course, introduction of the requirement for absorbent regeneration. Dissolved acid gases are removed from solution by pressure reduction and steam stripping as is conventional practice. In this configuration, the membrane $H_2S$ scrubbing process resembles a hot potassium carbonate plant in which the conventional packed tower absorber has been replaced by a membrane permeator. The advantages in this are enumerated below.

## APPARATUS

Figure 2 shows the apparatus used to measure membrane permeability. A membrane is placed in the test cell, and the test cell is inserted into an oven set at the desired operating temperature, usually from 90° to 130°C. Feed and sweep streams pass countercurrently over opposite sides of the membrane. The feed gas-- a mixture of $H_2S$, $CO_2$, $N_2$, and sometimes small amounts of other gases--is humidified by sparging through a boiler set at the temperature corresponding to the water pressure of the membrane liquid. Helium is likewise humidified and serves to meter the sweep steam. Flow rates of all streams are measured and gas compositions determined by chromatography. In liquid sweeping runs, a sweep liquid stream of appropriate composition pressurized by a metering pump replaces the low pressure sweep gas mixture of helium and steam.

While most tests have employed synthetic coal gas mixtures made from bottled gases, experiments have also been performed with actual coal gas. Coal gas supply pressure has been limited to one atmosphere to date.

## $H_2S$ MEMBRANE CHARACTERIZATION

The optimum operating temperature of the membrane is in the range of 90°C to 110°C, which coincides with that of the hot potassium carbonate systems. Total feed gas pressure is usually maintained at 300 psig--a typical operating pressure for fixed bed gasifiers. Inlet $H_2S$ partial pressures are representative of gasification of high sulfur coals--2.5 to 3.5 psi.

Figure 3 shows the dependence of membrane $H_2S$ permeability on the partial pressure of $CO_2$ in the feed gas. The inlet $H_2S$ partial pressure was 2.8 psi, but since substantial amounts of $H_2S$ were removed from the feed gas stream, the $H_2S$ feed partial pressure varied several fold from package inlet to outlet and in certain instances significant $H_2S$ partial pressures were present in the sweep stream. These data demonstrate the strong depressing effect of $CO_2$ partial pressure on $H_2S$ permeability which results from competition of the two acid gases for the membrane carrier, the carbonate anion. Such an effect can be predicted qualitatively by the theory of facilitated transport, although a rigorous mathematical description would be extremely complex.

The $CO_2$ partial pressures of interest in low Btu coal gas range from about 15 to 30 psi, corresponding to an average permeability for $H_2S$ of 3000-4000 x $10^{-9}$cc(RTP)-cm/sec-cm$^2$-cmHg$\Delta$P. As a basis for comparison, the room temperature $H_2S$ permeability of dimethyl silicone

rubber, the most permeable polymeric membrane available, is $850 \times 10^{-9}$. Unlike silicone rubber, the immobilized liquid membrane is virtually perfectly selective for acid gases; other coal gas components cross the membrane by the solution;diffusion mechanism, and solubilities in the hot, very concentrated salt solution are quite low.

$H_2S$ permeability is essentially unchanged upon raising the operating temperature from 90 to 110°C, although an increase in $CO_2$ permeability results in a decreased selectivity for $H_2S$ over $CO_2$ at the higher temperature. $H_2S$ permeability is also relatively insensitive to carbonate solution concentration, apparently due to competing effects between higher carrier loading and decreased diffusivities and activity coefficients at the high concentrations employed.

The permeation coefficient for $H_2S$ also depends on its own partial pressure in addition to that of $CO_2$; in Figure 4, the feed gas $CO_2$ partial pressure has been fixed while $H_2S$ inlet concentration is varied. Since the extent of $H_2S$ removal from the feed gas was limited to 15-30%, accurate point values of $H_2S$ permeability were obtained. At high feed partial pressures of hydrogen sulfide, the membrane carrier mechanism is saturated--that is, the extent of the facilitation is limited by the availability of the carbonate carrier for reaction at the feed side of the membrane, and $H_2S$ permeability falls off sharply at high partial pressures. For $H_2S$ partial pressures below about 3 psi, the permeation coefficient increases modestly with decreasing reactant partial pressure. This saturation phenomenon is a general feature of facilitated transport systems. The performance of facilitated transport membranes is made more difficult to describe due to the dependence of permeation coefficient on permeant partial pressure. This contrasts with the relatively simple situation for polymeric membranes in which permeability is often a constant characteristic of the identity of the permeating gas but not its pressure.

Membrane permeability to $H_2S$ depends on sweep side acid gas partial pressures as well as on those in the feed gas. In the liquid sweep runs summarized in Figure 4, the extent of conversion of incoming carbonate sweep solution to the bicarbonate form was varied to simulate different degrees of absorbent regeneration in the steam stripping process. The calculated equilibrium $CO_2$ partial pressures exerted by the incompletely regenerated sweep liquid are shown in Figure 4. The two dashed lines indicate that $H_2S$ transport is further hindered by the presence of the competing permeant $CO_2$ on the sweep side of the membrane.

The presence of $H_2S$ in the sweep stream influences transmembrane flux in two ways--(1) by decreasing the $H_2S$ partial pressure difference across the membrane (i.e., the driving force for transport) and (2) by decreasing the facilitation factor due to the decreased concentration gradient in bisulfide and bicarbonate ions resulting from partial membrane liquid conversion by $H_2S$ in the sweep stream.

As observed earlier, the transport of carbon dioxide is also facilitated by the carbonate membrane system. An important difference between $H_2S$ and $CO_2$ facilitated transport is that, while the chemical reactions which augment $H_2S$ flux are sufficiently rapid that $H_2S$ transport is essentially diffusion rate limited, the reaction of

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CO$_2$ with the membrane liquid is relatively slow due to the sluggish kinetics of CO$_2$ hydrolysis. Hence, reaction rates as well as equilibria are important in determining the permeation rate of CO$_2$. The significance of the difference in reaction rates is that carbonate absorbents-- whether immobilized as liquid membranes or not--exhibit an apparent selectivity for absorption of H$_2$S in preference to CO$_2$, and membrane CO$_2$ permeability is much lower than that of H$_2$S.

The high degree of control which the membrane designer has over the gas-liquid interface permits him to further improve this inherent selectivity for absorption of H$_2$S over CO$_2$. Figure 5 shows how H$_2$S:CO$_2$ selectivity can be enhanced by splitting a given total membrane liquid film thickness into two or more liquid layers, each separated by a thin gas-filled space. This so-called "gas gap" is conveniently pro- vided by a layer of a suitable non-wetting microporous polymer mem- brane. The rate of H$_2$S transport, being diffusion-limited, depends only on the total thickness of the membrane liquid films acting as diffusion barriers. Since the mass transfer resistance to H$_2$S of the intervening gas gap is entirely negligible, the H$_2$S permeability is not effected by this arrangement of the membrane sandwich. In contrast, the transport rate of CO$_2$ is diminished by dividing the mem- brane liquid film into multiple layers, since the CO$_2$ flux is sensi- tive to the rate of the relatively slow chemical reaction between CO$_2$ and membrane liquid and since these slow reactions are forced to occur an additional time for each new gas-liquid interface which is created. According to this much oversimplified description, the CO$_2$ transport rate is approximately halved by a single gas gap, de- creased 3-fold with two gas gap interlayers, etc., with a correspond- ing increase in H$_2$S:CO$_2$ separation factor α at no cost in reduced H$_2$S permeability. It should be observed that the selectivity enhancement requires only that the CO$_2$ reaction be slow relative to that of H$_2$S, since competition between these two reactants for membrane carrier determines selectivity. The CO$_2$ absorption reaction might be fast compared to the diffusion process.

Figure 6 shows that this simple analysis describes experimental data quite adequately. The ratio of H$_2$S and CO$_2$ fluxes has been determined for three membrane sandwich configurations and plotted as a function of CO$_2$ partial pressure in the feed stream; inlet H$_2$S concentration was fixed. Multilayering is seen to improve H$_2$S:CO$_2$ selectivity as predicted by theory, as the spacing and slopes of the lines drawn through the three data sets indicate. With a double gas gap arrangement (three membrane liquid layers) and a synthetic coal gas feed containing 2.7 psi H$_2$S and 20 psi CO$_2$, the H$_2$S:CO$_2$ flux ratio is increased from about 0.5 (no gas gap) to 1.5, corresponding to a permeate composition enrichment from 33% to 60% H$_2$S in CO$_2$. Selectivity for H$_2$S absorption is particularly important for integrated combined cycle power generation from low Btu coal gas for reasons discussed below.

Permeation data such as the above are used in predicting the membrane area requirement for any given application. Since the permeability of facilitated transport membranes depends on reaction kinetics and equilibria, it is not possible to characterize membrane performance by a simple permeability "constant" as for polymeric mem- branes, and in fact the permeation constant varies significantly from permeator inlet to outlet in the following integration:

$$A = \int_0^{N_{H_2S}} \frac{dN_{H_2S}}{Pr_{H_2S}(P_{H_2S, F} - P_{H_2S,S})} = \frac{\delta \cdot F_t}{P_t} \int_{P_{H_2S,i}}^{P_{H_2S,o}} \frac{dP_{H_2S, F}}{Pr_{H_2S} \cdot \Delta P_{H_2S}}$$

where $F_t$ and $P_t$ are the volumetric flowrate and total pressure of the coal gas feed. The $H_2S$ partial pressure difference across the membrane is calculated by material balance. For typical applications involving desulfurization of low-Btu coal gas produced from high sulfur coal, a range of 1-2 ft² of membrane area per kilowatt of generating capacity is predicted.

## MEMBRANE $H_2S$ SCRUBBING OF LOW BTU GAS

The conceptual layout of a liquid swept membrane $H_2S$ scrubbing system is shown in Figure 7; it is very similar to the hot carbonate flowsheet with the exception of the replacement of the conventional absorber with the novel membrane permeator.

Many of the benefits of membrane $H_2S$ scrubbing in the combined cycle power plant are due to the controllable, high membrane selectivity for $H_2S$ absorption. Minimizing $CO_2$ removal increases the fuel gas mass flow to the gas turbine, decreases the turbine compressor air requirement, and thus increases the net shaft work delivered to the gas turbine generator. On the other hand, passage of large amounts of $CO_2$ through the $H_2S$ removal and sulfur conversion trains is to be avoided for a number of reasons.

The total amount of acid gas flowing through the sulfur removal and conversion trains is less, of course, for the more selective process; specifically, three times less acid gas must be processed on a molar basis if the product stream from the $H_2S$ stripper consists of 60% $H_2S$ in $CO_2$ rather than 20% $H_2S$. A decrease in the total amount of absorbed acid gases to be stripped from solution should reduce the stripping steam requirement. Since insufficient waste heat is available in the plant to raise all the low pressure stripping steam required, a portion must be extracted from the steam turbine at a penalty in reduced power output; this penalty is minimized by high membrane selectivity. In short, less gasification, heat recovery, and gas and steam turbine equipment need be purchased per megawatt of exported power when selective membrane scrubbing is employed, and power plant first costs are thus reduced by more effective use of the energy available in the coal gas. The net plant heat rate is also improved by routing $CO_2$ to the turbines, reflecting lower operating as well as first costs.

A final consideration as regards the power plant is that a number of $H_2S$ removal processes, including the membrane scrubber, employ concentrated solutions of alkali metal salts as absorbents. With conventional absorption columns, a possibility exists for alkali metal carryover due to entrainment or foaming. This is unacceptable in view of the extremely low gas turbine tolerance

for alkali metals in the fuel gas due to hot corrosion problems. The carbonate membrane solution, on the other hand, is quite effectively immobilized.

The high absorption selectivity afforded by membrane $H_2S$ scrubbing also results in equipment and utility savings in the $H_2S$ scrubbing process itself. Specifically, the effective absorbent carrying capacity for $H_2S$ increases with selectivity, and a reduced solution recirculation rate is possible at a savings in pumping power. Since gas and liquor flowrates are down, the size of the stripping column is decreased, and a smaller acid gas condenser duty follows from the reduced stripping steam consumption.

The relatively high absorption temperature of 90-110°C is an advantage relative to processes which operate nearer ambient. The higher the absorption temperature, the less heat exchange area and heat rejection capacity that is required in the fuels plant. Energy losses due to incomplete heat recovery are minimized and less polluted condensate is generated. By operating at somewhat higher absorption temperatures and living with increased $K_2CO_3$ makeup requirements, the alkaline membrane liquid should be capable of absorbing carbonyl sulfide, if required, and hydrolyzing it to $H_2S$ and $CO_2$ to facilitate its conversion to elemental sulfur in the Claus plant.

Finally, Claus plant capital cost is sensitive to $H_2S$ concentration in the acid gas feed. Above 50% $H_2S$, the less expensive partial combustion process may be employed; at lower $H_2S$ concentrations, the split-stream configuration is required in order to achieve stable combustion. Furthermore, since $H_2S$ conversion to elemental sulfur is limited by equilibrium considerations, sulfur conversion efficiency increases with $H_2S$ concentration for a given number of catalytic stages. Since the cost of the sulfur conversion plant will be as large as that of the $H_2S$ removal plant, substantial cost savings can be realized here.

## MEMBRANE LIFE

Because of the very severe operating environment of coal gas, an extensive life testing effort has been undertaken, focussing on the liquid swept membrane. The membrane has been operated at 90°C and a pressure of 300 psig with synthetic coal gas mixtures. Tests have also been performed on actual coal gas produced by the GEGAS-F atmospheric fixed bed gasifier. Both chemical and physical effects have been sought and solutions developed for membrane life-limiting problems as they have been identified. Promising life test results have been obtained which will soon be reported.

## CONCLUSIONS

The superior performance of facilitated transport immobilized liquid membranes makes possible the use of membranes to do industrially significant gas separations. The extremely high permeability and $H_2S:CO_2$ selectivity of carbonate liquid membranes

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makes them particularly suitable in low Btu coal gas-combined
cycle power plant applications.  In addition to high performance,
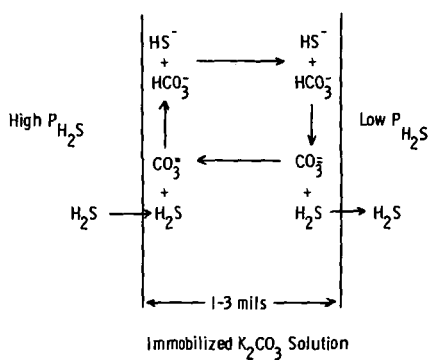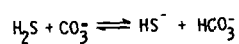reasonable membrane life is being demonstrated.

## ACKNOWLEDGEMENTS

## REFERENCES

(1)  Ward, W.J., Browall, W.R., Salemme, R.M., "Ultrathin
     Silicone/Polycarbonate Membranes for Gas Separation
     Processes", Journal of Membrane Science, 1, March, 1976.

(2)  Browall, W.R., Kimura, S.G., "Ultrathin Membranes for
     Oxygen Enrichment", Presented at VI Interamerican Congress
     of Chemical Engineers, July, 1975.

(3)  Kimura, S.G., Browall, W.R., "Permselective Membranes for
     Oxygen Enrichment", General Electric Publication, 1976.

(4)  Ward, W.J., "Immobilized Liquid Membranes" from Recent
     Developments in Separation Science, N. Li ed., Chemical
     Rubber Company, 1974.

(5)  Stein, W.D., The Movement of Molecules Across Cell Membranes,
     Academic Press, 1967.

(6)  Ward, W.J., Robb, W.L., "Carbon Dioxide-Oxygen Separation:
     Facilitated Transport of Carbon Dioxide Across a Liquid
     Film" Science, 156, 3781, June 16, 1967.

(7)  Ward, W.J. "Analytical and Experimental Studies of Facilitated
     Transport" AIChE Journal, 16, 3, May, 1970.

(8)  Schultz, J.S., Goddard, J.D., Suchdeo, S.R., "Facilitated
     Transport Via Carrier Mediated Diffusion in Membranes"
     AIChE Journal, 20, 3, May, 1974 and 20, 4, June, 1974.

(9)  Tosh, J.S., Field, J.H., Benson, H.E., and Haynes, W.P.,
     "Equilibrium Study of the System $K_2CO_3$, $KHCO_3$, $CO_2$, and $H_2O$,
     U.S. Bureau of Mines, Report of Investigations 5484, 1959.

FIGURE 1.
FACILITATED TRANSPORT OF HYDROGEN SULFIDE

$$H_2S + CO_3^= \rightleftharpoons HS^- + HCO_3^-$$



SIMILAR REACTION FOR FACILITATED TRANSPORT OF $CO_2$

$$CO_2 + CO_3^= + H_2O \rightleftharpoons 2HCO_3^-$$

FIGURE 2.

PERMEATION TEST SYSTEM



FIGURE 3.

## EFFECT OF CO_2 PARTIAL PRESSURE ON H_2S PERMEABILITY
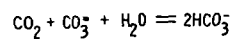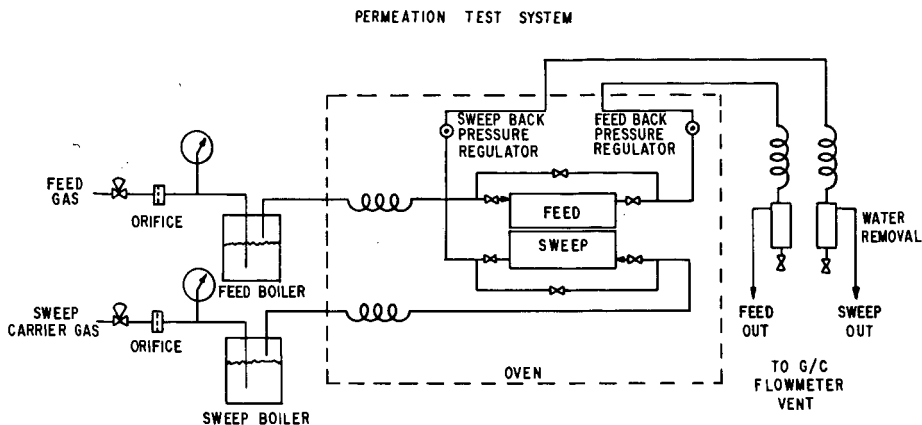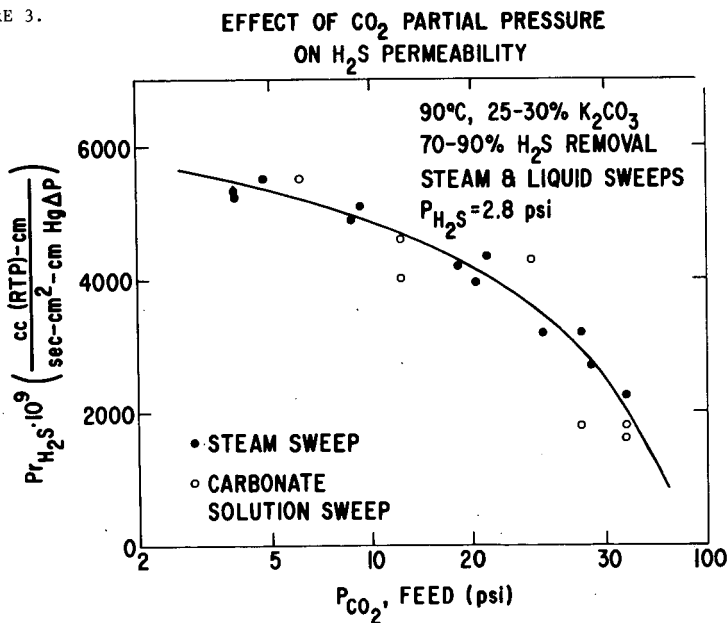
## FIGURE 4.

### $H_2S$ PERMEABILITY MAP AT 90°C, 30 PSI $CO_2$ IN FEED

25% $K_2CO_3$, 90°C

$P_{CO_2}$, FEED=30 psi

$Pr_{H_2S} \cdot 10^9 \left( \dfrac{cc\ (RTP)-cm}{sec-cm^2-cm\ Hg\Delta P} \right)$

$P_{H_2S}$, FEED (psi)

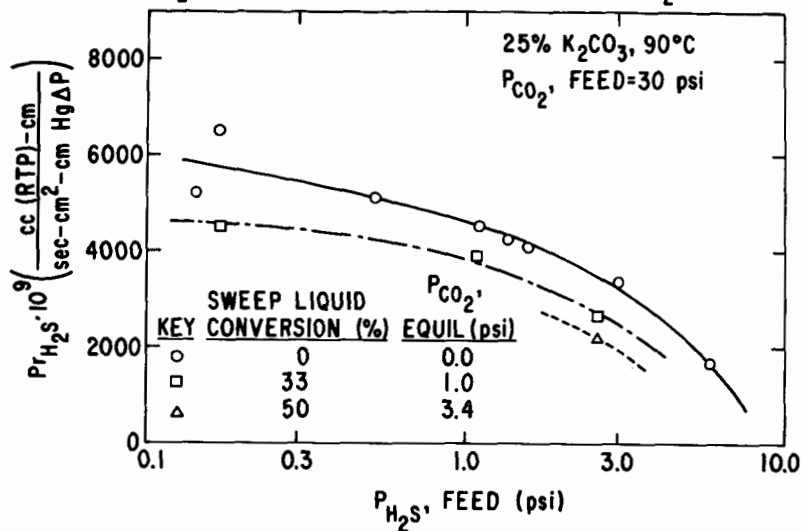| KEY | SWEEP LIQUID CONVERSION (%) | $P_{CO_2}$, EQUIL (psi) |
|-----|-----------------------------|-------------------------|
| ○   | 0                           | 0.0                     |
| □   | 33                          | 1.0                     |
| △   | 50                          | 3.4                     |

## FIGURE 5.

### IMPROVEMENT OF $H_2S/CO_2$ SELECTIVITY BY GAS GAP
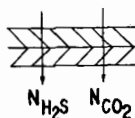
DIFFUSION LIMITED $H_2S$ TRANSPORT:

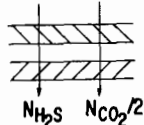$$N_{H_2S} \propto \frac{1}{(\text{TOTAL LIQUID FILM THICKNESS})}$$

REACTION RATE LIMITED $CO_2$ TRANSPORT:

$$N_{CO_2} \propto \frac{1}{(\text{NUMBER OF GAS-LIQUID INTERFACES})}$$

I. TWO ILM'S IN CONTACT

II. TWO ILM'S SEPARATED BY GAS GAP

$N_{H_2S}$  $N_{CO_2}$

$N_{H_2S}$  $N_{CO_2}/2$

$$\therefore \ \alpha_{II} \approx 2\alpha_{I}$$

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FIGURE 6.

ENHANCEMENT OF MEMBRANE $H_2S/CO_2$
SELECTIVITY BY GAS GAP



90°C, 30% $K_2CO_3$
70-90% $H_2S$ REMOVAL
$P_{H_2S} = 2.7$ psia

H$_2$S/CO$_2$ FLUX RATIO

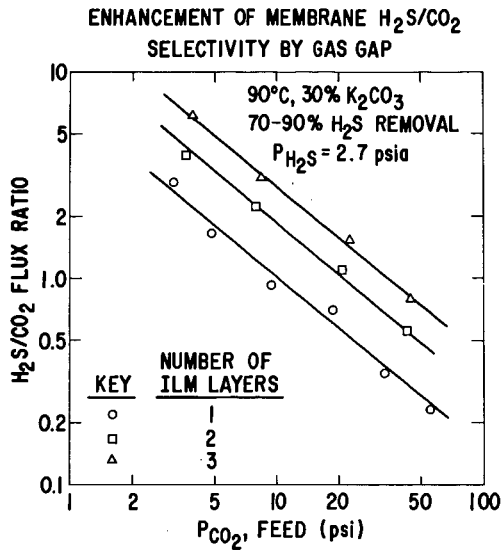| KEY | NUMBER OF ILM LAYERS |
|-----|----------------------|
| ○ | 1 |
| □ | 2 |
| △ | 3 |

$P_{CO_2}$, FEED (psi)

FIGURE 7.

MEMBRANE $H_2S$ SCRUBBING SYSTEM
(LIQUID SWEEPING)



CW

$H_2S$ & $CO_2$
TO
CLAUS UNIT

CLEAN
COAL GAS

STRIPPING
COLUMN

COAL GAS
+ $H_2S$

SWEEP LIQUID

STEAM

MEMBRANE
PERMEATOR

77